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AUGMENTING A MICROBIAL SELECTIVE PLUGGING TECHNIQUE WITH POLYMER FLOODING TO INCREASE THE EFFICIENCY OF OIL RECOVERY - A SEARCH FOR SYNERGY

THIRD SEMI-ANNUAL PROGRESS REPORT

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ABSTRACT

The overall objective of this project is to improve the effectiveness of a microbial selective plugging technique (MPPM) through the use of polymer floods. Of the six tasks to be carried out, one (Task 2) was scheduled to be completed, two (Tasks 1 and 3) were scheduled to continue, and one (Task 4) was to begin. A new (at this time proprietary) polymer solution is being prepared by Dr. Hester at the University of Southern Mississippi for testing in our project.

Sandpack studies have demonstrated that the injection of both polymer solutions and microbial nutrients cause an alteration of the flow pattern through the pack.

Core flood studies using Berea sandstone cores have begun. The opportunity to enhance the value of the information derived from these studies through cooperation with Dr. Watson at Texas A&M are being pursued. Preliminary results using MRI have shown the necessity to modify our protocol and plans are now being formulated.

INTRODUCTION

Over two thirds of all of the oil discovered in this country is still in the ground and cannot be recovered economically with present day technology. Only 27 billion barrels of the approximately 345 billion barrels remaining in known reservoirs is economically recoverable. When primary production becomes uneconomical, secondary and tertiary methods, such as waterflooding, chemical flooding, CO_2 or N_2 flooding, and microbial enhanced oil recovery (MEOR) are employed. Recently, a microbial permeability profile modification (MPPM) procedure was shown to be a cost effective means of enhancing oil recovery.[(1)] In fact, aside from waterflooding alone, MPPM is the least expensive of the enhanced oil recovery procedures. Since MPPM and permeability modification via polymers are similar in mode of action, it was reasoned that coupling those two technologies might result in a synergy that is not only cost effective but also more efficient in oil recovering.

Dr. Alex Vadie, retired from the University in September 2000 but will continue to act in an advisory capacity for the remainder of the project. Dr. F. Leo Lynch, a geologist, has been added to the scientific team and J. E. Parker, a retired petroleum engineer has assumed a more prominent role in the core flood work being conducted on the project.

RESULTS AND DISCUSSION

Objective

The overall objective of this project is to improve the effectiveness of a microbial selective plugging technique of improving oil recovery through the use of polymer floods. More specifically, the intent is to increase the total amount of oil recovered and to reduce the cost per barrel of incremental oil. In order to accomplish these objectives, the following six tasks will be carried out.

Task 1. Select, characterize, and test various polymers for their impact on the microflora indigenous to petroleum reservoirs in terms of their inhibitory capabilities and their biodegradability.

Task 2. Determine the ability of selected polymers to increase the aerial extent (aerial sweep efficiency) of stratal material colonized by microorganisms in sandpacks.

Task 3. Determine the ability of selected polymer flooding protocols in combination with microbial selective plugging techniques to increase oil recovery from Berea sandstone core plugs prepared to mimic a depleted oil sand.

Task 4. Determine the ability of a microbial selective plugging technique in combination with selected polymer flooding protocols to increase oil recovery from live cores obtained from newly drilled wells.

Task 5. Prepare a cost/benefit evaluation of adding a polymer-flooding procedure to a microbial enhanced oil recovery process using a selective plugging technique.

Task 6. Final report preparation.

Results

To facilitate presentation of accomplishments on this project, results will be set forth by task.

Task 1. Select, characterize, and test various polymers for their impact on the microflora indigenous to petroleum reservoirs in terms of their inhibitory capabilities and their biodegradability.

No new polymers have been obtained and thus no new studies on this task were conducted during this six month period. However, arrangements have been made with Dr. Hester (University of Southern Mississippi) to supply a polymer solution. Dr. Hester is developing an as yet proprietary group of polymers (DOE/NPTO grant) which exhibit very large extensional viscosities relative to their shear-based viscosities. As these polymers extend in the direction of flow when subjected to shear, they absorb energy. It is postulated these polymers might be unusually effective at redistributing water flow in porous media from regions of higher flow velocities to those of lower velocities. We will experiment with these upon there receipt from Dr. Hester.

Task 2. Determine the ability of selected polymers to increase the aerial extent (aerial sweep efficiency) of stratal material colonized by microorganisms in sandpacks.

Work on this task essentially has been completed but will probably be continued when new polymers are obtained and there is reason to believe they may respond differently. In order to make the results obtained during this reporting period understandable, a brief recitation of the methodology employed will be presented.

The packing material in a majority of the sandpacks was 95 g crushed Berea sandstone, 5 g clay, 11 g oil-microorganism mixture, and 8 ml simulated injection water.

Prior to use in an experiment, simulated injection water (hereinafter referred to as water) is allowed to flow through the sandpack to establish a flow path. The water is allowed to flow through the pack using only the pressure achieved by having the water reservoir situated three feet above the pack.

The injection water employed to track the path of the water through the pack was prepared as follows.   The following ingredients were dissolved separately in 2 liters of distilled water: 10.9 g of $CaCl_2$, 2.71g of $MgCl_2$, 4.57g of $BaCl_2$, 1.84 g of Na_2SO_4, and 147.8 g of NaCl. Once dissolved, the solutions were mixed in a 50 liter carboy. The volume of this solution was adjusted to 50 l using distilled water. The pH of the injection water was adjusted to 7.0 using a 10%(v/v) HCl solution. ^{56}Mn, generated on site, is added to the injection water and the pathway of flow throught the pack determined. After the path of the water through the pack has been established, a polymer solution is injected and the path of the injection water again determined using the ^{56}Mn solution described above.

The polymer classes tested were a polyacrylamide (Alcoflood 1285), a cross-linking polymer (Alcoflood 254s), and a xanthan polymer (Flocon 4800). All three classes of polymers were able to alter the path of the injection water as may be seen in Figures 1, 2, and 3. The Alcoflood 1285 polymer began altering the flow of injection water at the source of injection while the Alcoflood 254s and Flocon 4800 altered the flow after moving at least 3 cm into the pack. This is believed to be due to the fact that the Alcoflood 1285 was more viscous than the other polymers at the concentrations tested. After the flow of injection water had been established, the packs were supplemented with nitrogen and phosphorous.

The addition of a nitrogen source and a phosphorous source encouraged the growth of microorganisms in the newly polymer-established injection water paths resulting in these paths being altered (Figures 1, 2, and 3). Control packs not receiving polymer or microbial nutrients were setup to determine if the path of injection water could be altered by repeated water floodings. The control packs showed that repeated water floodings would not alter the flow of the injection water.

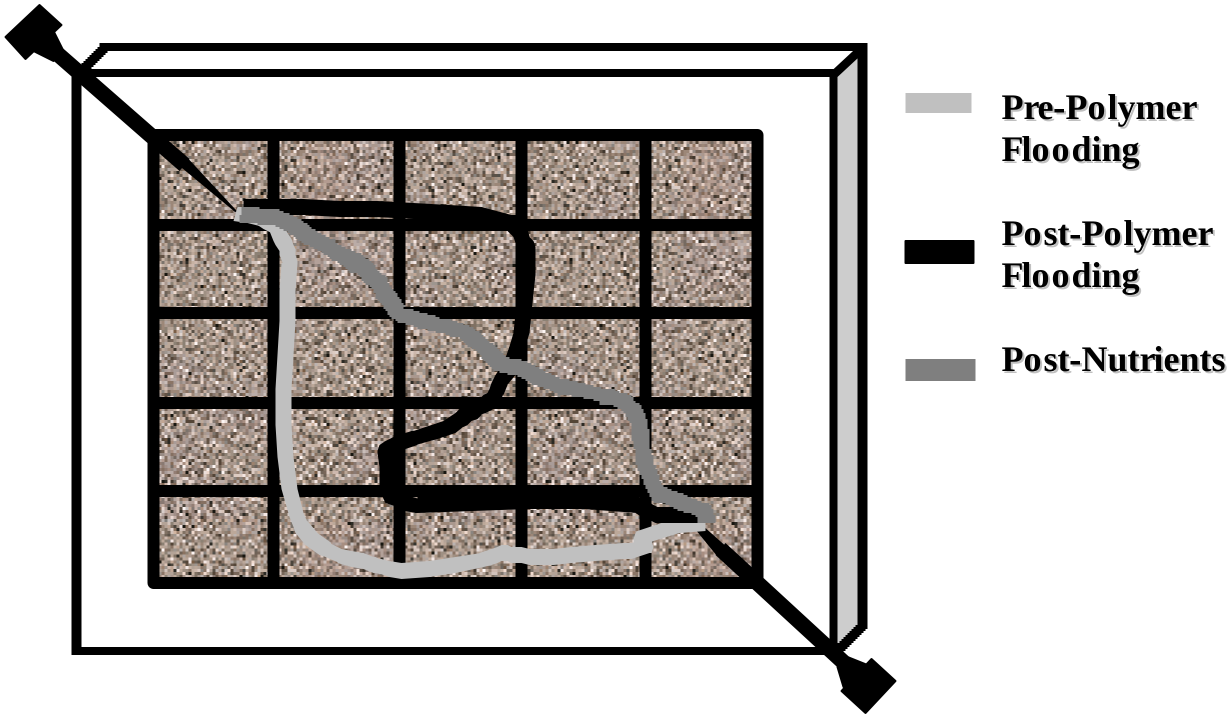

Figure 1. Sandpack 03-21-00-01 treated with Alcoflood 1285 and later with nutrients.

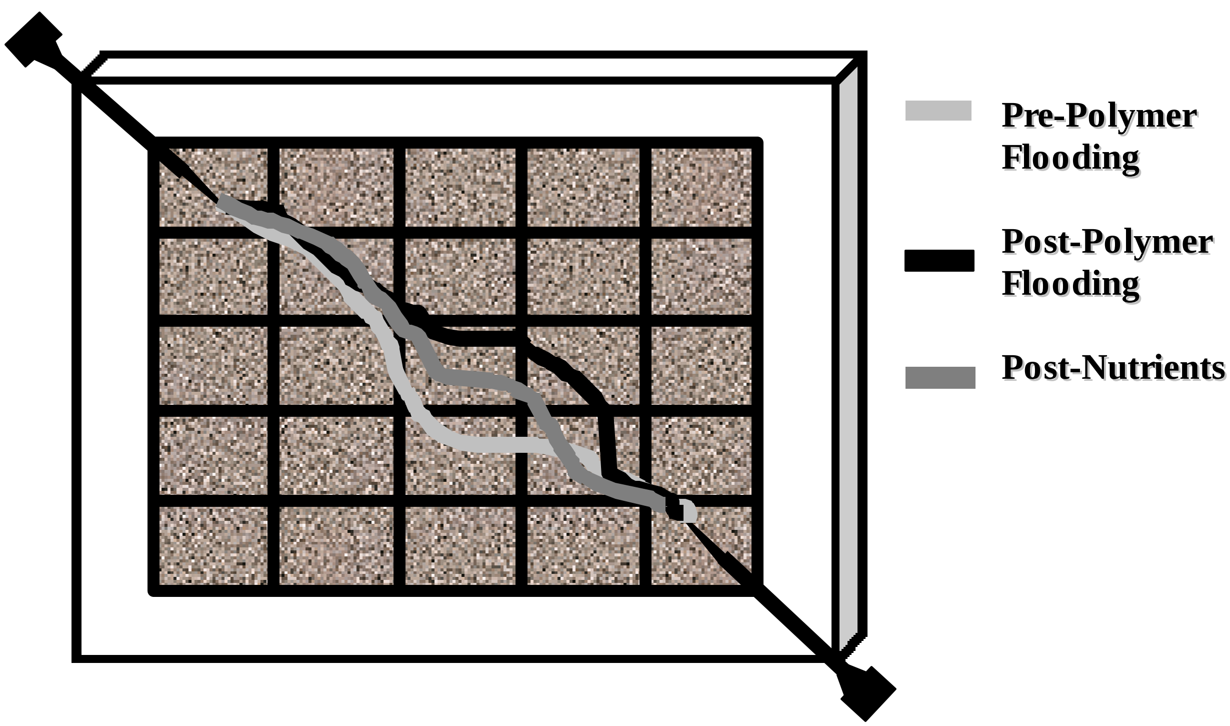

Figure 2. Sandpack 05-08-00-01 treated with crosslinking polymer and later with nutrients.

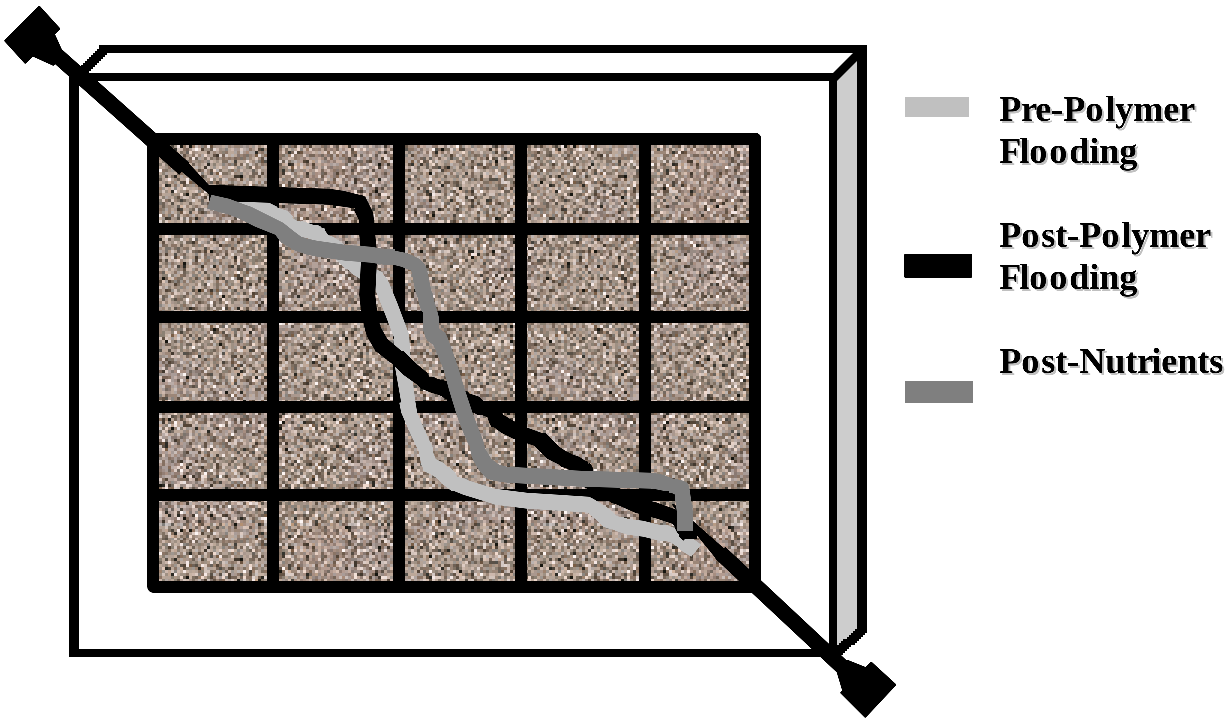

Figure 3. Sandpack 06-28-00-01 treated with Flocon 4800 and later with nutrients.

Task 3. Determine the ability of selected polymer flooding protocols in combination with microbial selective plugging techniques to increase oil recovery from Berea sandstone core plugs prepared to mimic a depleted oil sand.

The assembly prepared to test polymer flooding and microbial growth was shown in the last progress report and several cores prepared to mimic a depleted oil sand. A core was placed in a vacuum chamber, evacuated, and filled with injection water. The water-saturated core was placed in the core flood assembly and injection water flowed through the core. Crude oil from the North

Blowhorn Oil Field then was flowed through the core until no more water was present in the effluent. Injection water was again flowed through the core until no more oil was present. At this point, the core is considered equivalent to a depleted oil sand.

Preliminary experiments demonstrated that the injection of a polymer solution through the core (prepared to simulate a depleted oil sand) resulted in the recovery of oil from the core. Similarly, when the injection water was supplemented with microbial nutrients (potassium nitrate and disodium hydrogen phosphate) additional oil was observed in the effluent several days after the injections.

The original plan was to alternate the polymer and nutrient injections in the search for synergy with the main criterion for success being the recovery of oil from the cores. However, at the contractor's meeting held in Denver in June, Gary Walker (DOE) suggested several individuals to contact in regard to techniques being used by others to increase the amount of information we can obtain in our core experiments. Accordingly, we discussed our proposed experiments with Dr. Ted Watson of Texas A&M who conducted a preliminary experiment for us as described below.

MRI Studies

The first attempts have been made to image oil-depleted Berea sandstone core by NMR using a GE2-Tesla CSI-II imager/spectrometer with a 31 cm magnet bore. This spectrometer is equipped with a 20G/cm shielded gradient-coil set and a birdcage RF coil. The work was performed at Texas A&M University in cooperation with Professor Ted Watson (also a DOE/NPTO grant holder). The key question was: can regions of H_2O versus regions of oil clearly be imaged using ^1H NMR? If successful, the three-dimensional images would permit us to directly observe at high resolution the locations of oil versus water throughout the core and follow these as a function of both polymer/water flooding and water flooding after microbial growth. Thus, a direct observation could be made of water redistribution patterns and oil migration upon (a) polymer flooding, (b) MEOR experiments, or (c) synergism between polymer flooding and MEOR.

The following suite of experiments were performed on two Berea sandstone cores (about 3.5 in. long and 1.25 in. dia.).

Core 1. A core was prepared as described above using oil from the North Blowhorn Creek oil field/Lamar Co. AL (API gravity 28-35.2) .

Core 2. This core was identical to Core 1 except that it was subsequently treated with a polymer flood where 255 ml (12-14 core void volumes) of a polymer solution (Alcoflood 1285, mol. Wt. ~ 20,000,000: 75 mg per liter of standard brine solution) was pumped through the core.

The cores were:

(a) Profile imaged along longitudinal axis

(b) Two-dimensional images were made (horizontal slices of 5 mm thickness taken)

(c) Inversion recovery (T_1) experiments were done

(d) NMR ^{1}H spectrum were taken. Also, inversion recovery experiments were done on both oil and water.

These experiments proved unable to distinguish between the oil and water regions of the cores due to severe line-broadening associated with the Berea sandstone. This can be seen in Fig. 4 where a broad ^{1}H line width of ~2000 Hz was obtained. This width is much larger than the 300 Hz (at

85 MHz) chemical shift difference between the protons in oil (e.g. C-H) and the protons in water (e.g. O-H). This means we need to reduce the line broadening. Berea sandstone is particularly bad in this respect but, when we use cores from the North Blowhorn Creek field, this problem may be reduced.

Figure 5 shows a one-dimensional profile of the ^{1}H signal intensity across the length of the Core 1 at a pixel size of 0.47 mm. A similar profile of Core 2 shows some fluid loss from one end of the polymer-flooded sample (Figure 6). Two-dimensional images are shown in Figures 7 and 8 for Cores 1 and 2, respectively. These images are of a 5 mm thick slices taken directly down the center of the axes. The brightened areas indicate greater concentrations of ^{1}H nuclei (e.g. oil and water). The dark areas are rock. Once we are successful at resolving oil and water regions we will be able to see oil and water distributions on scale similar to that shown in these images.

Inversion-recovery experiments are shown for the oil sample and for Cores 1 and 2 in Figure 9.

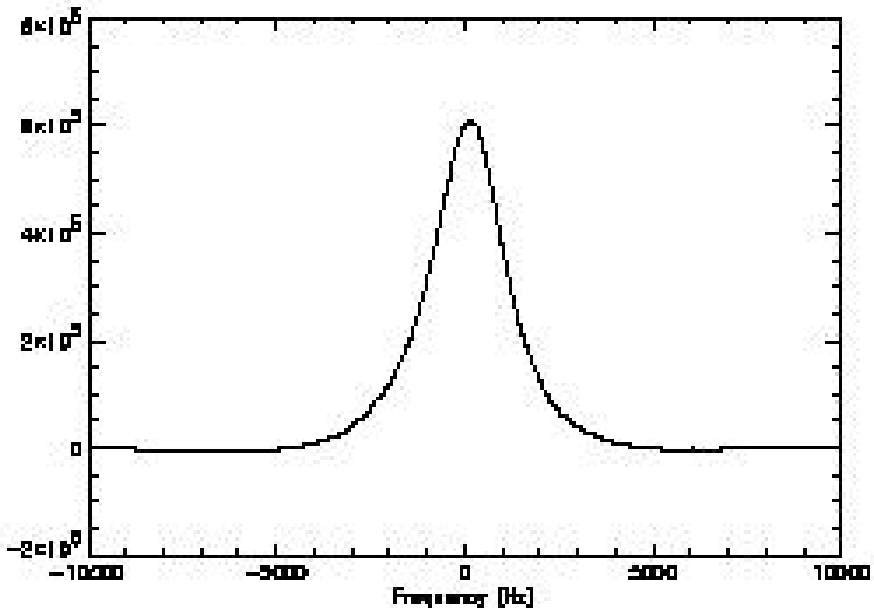

Figure 4. NMR spectrum of sample #1.

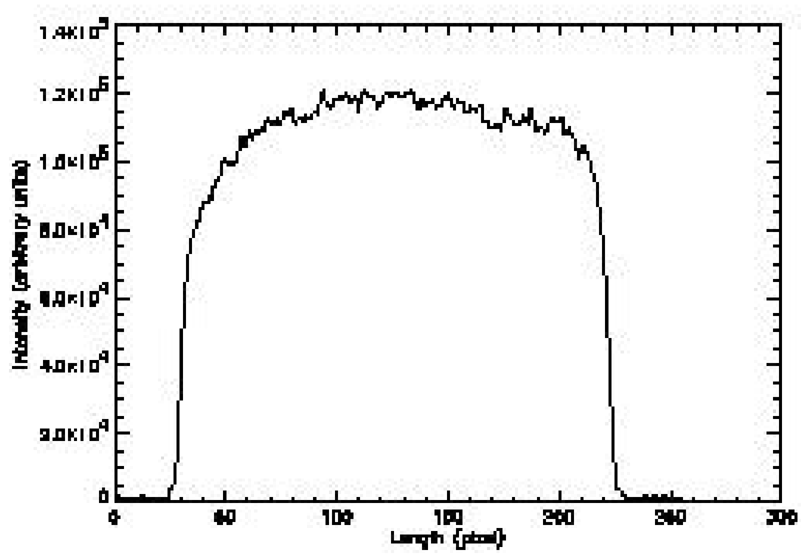

Figure 5. 1-D profile of sample #1. The pixel size is 0.47 mm.

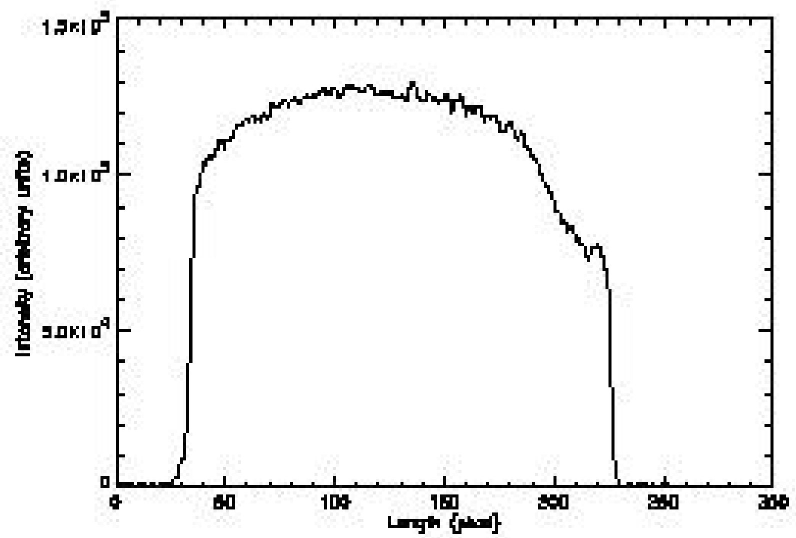

Figure 6. 1-D profile of sample #2. The pixel size is 0.47 mm.

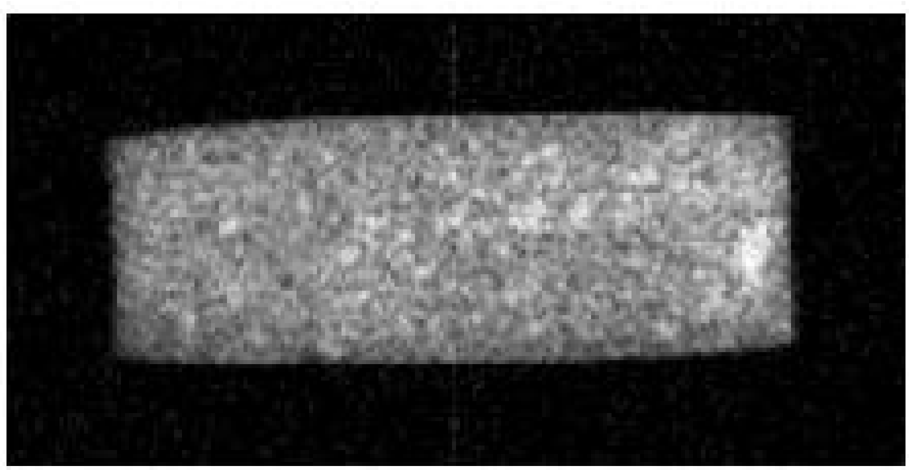

Figure 7. 2-D image of sample #1.

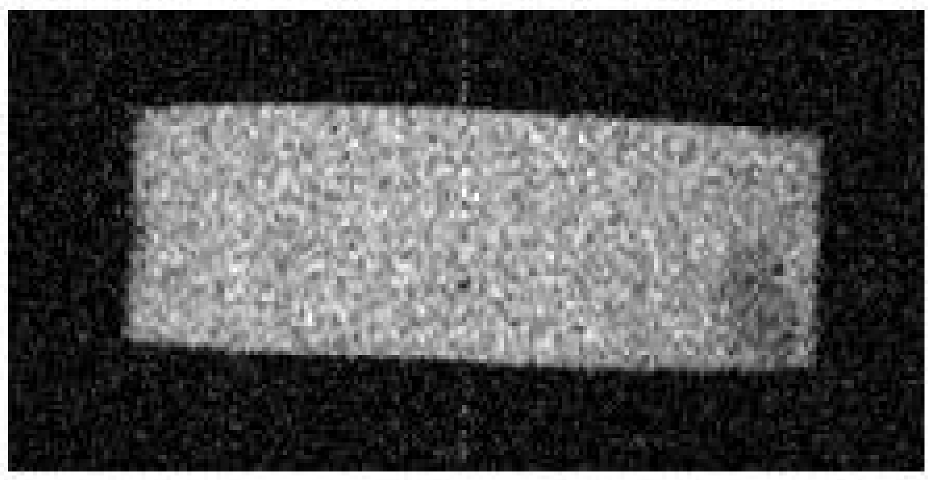

Figure 8. 2-D image of sample #2.

Proton relaxation in oil occurs at a different rate in the core versus in bulk. This may simply reflect the signal in the core which is representing both oil and water. The relaxation characteristics of Cores 1 and 2 differed. The calculated relaxation distributions are shown in Figure 10. The tall peak in Core 1 belongs to water.

There are several ways we plan to get oil/water contrast so as to clearly follow changes in water and oil distributions in cores as a function of treatments in the future. Use D_2O instead of H_2O. Thus, only the oil protons will be seen and oil distribution will be clearly imaged.

1. Use different rock samples. For example carbonate rocks have narrow line widths. Bentheimer sandstone could be used. In live core experiments, the rock from the

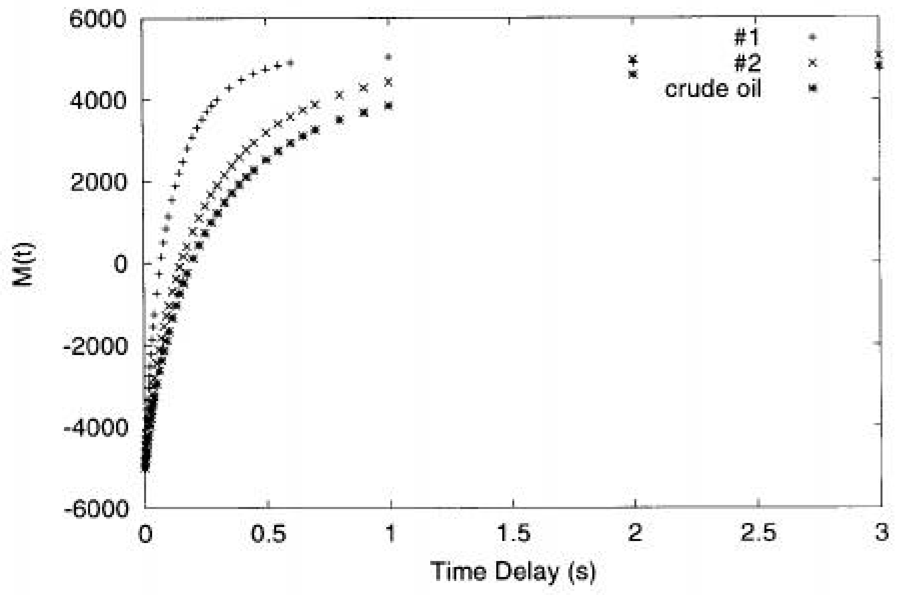

Figure 9. Inversion-recovery T_1 data for the core samples and oil.

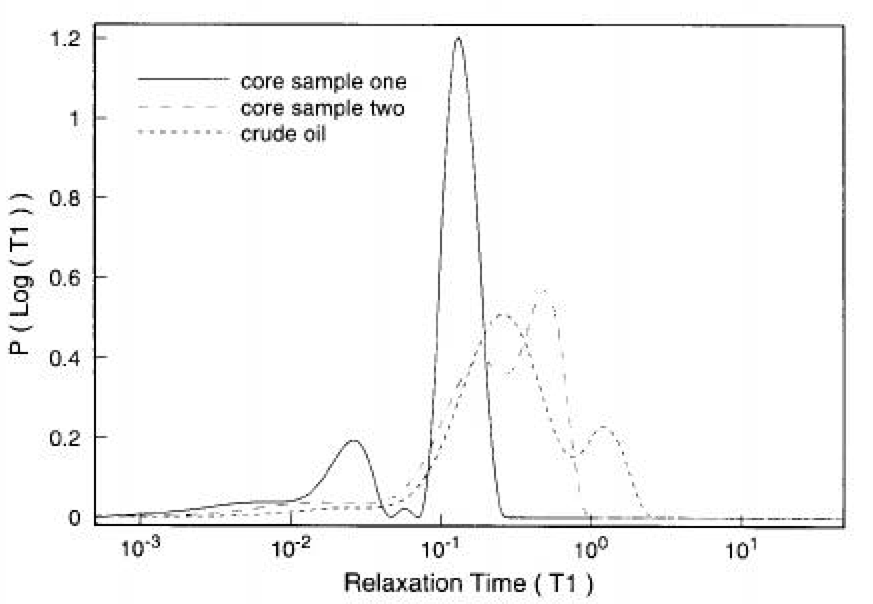

Figure 10. T_1 distributions for the core samples and oil.

North Blowhorn Creek field could be better.

3. Image water using Na-23 (a large amount of Na is present in the brine solution used so water location, independent of oil, could be followed).

4. Add tiny amounts of EDTA to the water used so that the water relaxation time is changed.

<u>Studies of Alcoflood 1285 (Mwt~20,000,000) Water Solutions in Berea Cores.</u>

Alcoflood 1285 is an acrylamide polymer with 25% of the monomer units hydrolyzed to carboxyl salt groups that is being used to assist oil recovery from oil depleted cores and to evaluate its effect on MEOR. It was decided to see if this polymer will (1) be adsorbed by Berea cores or (2) undergo shear degradation which lowers the molecular weight while.

The method used to study these possibilities was viscosity monitoring. Since Alcoflood is used in such a dilute solution (0.3mg to 2mg per liter of water), it is impossible to use polymer recovery experiments after pumping solutions through cores to measure weight losses. Therefore, viscosity studies were used.

Standard brine solutions were made and their viscosities were measured. Then polymer concentrations of 0.75mg polymer/liter were made. The polymer solution was taken up into an evacuated Berea core with an initial pore volume of about 17-20 ml. After sitting submerged for several hours, the core was rigged for pumping the same polymer/water solution through it. Then several liters of polymer solution were pumped through the core at a constant rate. The rate was controlled by the pressure differential between the reservoir (head) pressure and the backpressure regulator at the outlet end of the system.

The viscosity of the brine solution was compared to that of the starting polymer/brine solution, the viscosity of the first 25 ml of polymer/brine solution to be pumped out of the core and the viscosity of polymer/brine solutions after more extended amounts were pumped through the core. This same experiment was then repeated a second time at higher flow rates (higher shear conditions). These results are presented in Table 1 where the viscosities are simply represented as the time for a standard amount of solution to flow through the Cannon Ubbeholde Viscometer. The longer the flow time, the higher the viscosity.

Table 1: Viscosities of Brine and Polymer Solutions and Viscosities of Polymer Solutions After Pumping Through a Berea Core.

	Exp. 1 Flow Rate = 0.034 ml/sec	Exp.2 Flow Rate = 0.213 ml/sec
Brine Solution: ($_o$ sec)	99	99
Brine/Polymer (starting solution)	130.9	125.7
First 25 ml from core	98.5	124.7
Middle Sample		
(at 2455 ml pumped)	114.0	
(at 850 ml pumped)		116.0
Final Sample		
(at 3226 ml pumped)	115.3	
(at 1700 ml pumped)		113.3

* In both experiments a polymer concentration of 0.75 mg of 1285 per liter of brine was used.

When the core is first filled with polymer solution, essentially all of the polymer is adsorbed on the internal Berea core surfaces. This can be seen by comparing the viscosity of the first ~1.5 core vol. of solution to be pumped out (25 ml vs ~17 ml pore vol.). The initial polymer solution viscosity of 130.9 has dropped to 98.5, which is essentially the same as that of pure brine solution (99 sec). Thus, the polymer present in that volume of solution has been adsorbed. After pumping 2455 ml through (e.g. 144 core pore volumes), the viscosity of the exiting polymer was 114. This remained the same after 3226 ml (190 core void volumes) were pumped through (e.g. 115.3). Thus, all the internal pore volume surfaces have reached equilibrium-coating levels. We suggest the difference in viscosity between the original polymer solution and that pumped out much later (130.9 – 114 = 16.9) is due to shear degradation.

In the second experiment, the first 1.5 core void volume pumped out of the core had the same viscosity as that of the initially made polymer solution (125.7 and 124.7, respectively). This contrasts sharply with the first experiment but is completely logical. In the first experiment, the core surfaces had never previously been exposed to polymer. This same core, however, was used in the second experiment. By that time it had had 3226 ml of polymer solution pumped through it (e.g. 2.42 mg of polymer solution had been pumped into the core before experiment 2 had started). Thus, when experiment 2 began, the core surfaces had already adsorbed all the polymer they could hold. After 850 ml and 1700 ml of polymer solution had been pumped through (experiment 2) the viscosities (115 and 113.3) were the same as those seen at the middle and end of experiment one (114.0 and 115.3, respectively). Thus, we suggest shear degradation during flow through the core probably accounted for the difference in the viscosity between the initial polymer solution and that pumped through the core. However, if shear degradation accounts for this drop, the amount of shear degradation in the experiments 2 and 1 were essentially the same despite the fact the flow rate in the second experiment was about 6.3 times greater.

Task 4. Determine the ability of microbial selective plugging technique in combination with selected polymer flooding protocols to increase oil recovery from live cores obtained from newly drilled wells.

Work on this phase of the project has been delayed somewhat due to the highly encouraging opportunity of making these experiments significantly more meaningful by the potential results from the core analyses being designed in concert with Dr. Watson of Texas A&M.

Attempts to obtain new cores from recently drilled wells have not been successful and cores from previously drilled wells are unsatisfactory due to the method of storage since being obtained. This potential problem was foreseen and contingency plans put in place earlier. Cores obtained from the last DOE project have been preserved under nitrogen will be employed for the live core experiments. These cores are in as close to their original state as possible and do contain indigenous microorganisms in their native state. If, however, opportunities to obtain additional new cores arises, they will be obtained and used also.

Task 5. Prepare a cost/benefit evaluation of adding a polymer-flooding procedure to a microbial enhanced oil recovery process using a selective plugging technique.

Not scheduled.

Task 6. Final report preparation.

Not scheduled.

SUMMARY AND CONCLUSIONS

No new polymers were obtained for testing during this reporting period, but arrangements have been made to obtain samples of a proprietary polymer from another DOE contractor (Dr. Hester at the University of Southern Mississippi).

Sandpack studies have clearly shown that both polymer solutions and flooding with microbial nutrients alter the flow path of injection water through the sandpacks.

Two Berea sandstone cores prepared to simulate a depleted oil-sand (one treated with a polymer solution) were examined by Dr. Ted Watson of Texas A&M using MRI. Several problems with using Berea sandstone became evident and recommendations to correct the problem are being investigated. Plans for additional studies are being formulated.

REFERENCES

1. Stephens, J.O., L.R. Brown, and A. Alex Vadie. 1999. The Utilization of the Microflora Indigenous to and Present in Oil-Bearing Formations to Selectively Plug the More Porous Zones Thereby Increasing Oil Recovery During Waterflooding. DOE contract DE-FC22-94BC14962.